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OPTICAL, ADDITIONAL FILMS AND OPTICAL ELEMENTS

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BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to optical, additional films suitably used, for example, in vacuum ultraviolet lithography, particularly, in F₂ laser lithography, optical elements in which the optical, additional film or films are added on a substrate, and *an*
10 optical apparatus using the optical element or elements.

 The optical, additional films herein are, *for example,* ~~such~~
~~films as~~ antireflection coatings, reflective coatings, or protective coatings, formed on surfaces of optical
15 elements.

Related Background Art

~~Concerning the~~ ^C conventional i-line (wavelength 365 nm) and KrF laser (wavelength 248 nm) lithographies, glass materials for ~~such~~ optical elements ^{such} as lenses,
20 antireflection coating materials, environments, etc. that were applicable to optic ^{al} systems of optical apparatus ^o, ^a such as ^a projection exposure apparatus, illumination apparatus, measuring apparatus, etc., used in ~~such~~ lithographies, were a direct extension of the
25 conventional technologies and ~~were able to be prepared~~ ^{could} by ~~application of the~~ ^{methods} conventional technologies.

 As for the lithography in the vacuum ultraviolet

region, however, oxygen, water, etc. ^{strongly} ~~greatly~~ absorbs light, ^{Thus,} ~~and it is thus~~ necessary to keep an atmosphere under vacuum or to replace ^{it} ~~an atmosphere~~ with ^a gas such as nitrogen or helium.

5 In the ArF laser lithography at the wavelength of 193 nm, conventionally used silica and fluorite were applicable as glass materials and antireflection coating materials and it was also possible to select certain kinds of metal fluorides and oxides.

10 Silica (SiO_2) has been used heretofore as a material for optical elements for ^{an} ArF laser. It was because silica (SiO_2) ^{has a} ~~had the~~ high transmittance of 90% for ^{an} ArF excimer laser light and ^{is} ~~possessed the~~ stable ^{an} ~~property against~~ variations in temperature, humidity, ^{upon} and so on. However, the transmittance of silica (SiO_2) ^{is substantially lower} ~~becomes extremely lowered~~ for the F_2 laser light having the wavelength of 157 nm, and it is impossible to use ^{silica} ~~it~~ as an optical material.

20 On the other hand, in the F_2 laser lithography, only fluorite (CaF_2) is applicable as a glass material capable of sufficiently transmitting rays at the wavelength of 157 nm, which ^{is the} ~~is hindrance to~~ design of optical systems.

25 Further, the F_2 laser lithography also involves a problem concerning ~~the~~ optical, additional films, such as the antireflection coatings or the like. In general, the antireflection coatings are formed in ^a ~~multilayer~~

structure of ^a combination of a material having a
refractive index smaller than that of ~~a material of a~~ ^{the}
substrate with a material having a refractive index
higher than that of the ~~material of the~~ substrate,
5 thereby yielding a stronger antireflection effect than
that of the antireflection coatings of ^a ~~a~~ monolayer
structure.

However, no material with a refractive index
higher than that of fluorite has ^{yet} been found ~~yet~~ as a
10 material for antireflection coatings, so that magnesium
fluoride (MgF_2) or lithium fluoride (LiF) with the
refractive index lower than that of fluorite had to be
used in monolayer structures in the F_2 laser lithography.
^{Therefore} Under such circumstances, there ^{is a need} ~~are desires~~ for a
15 material having a refractive index higher than that of
fluorite and being capable of making the optical,
additional films (antireflection coatings, reflective
coatings, protective coatings) of ^a multilayer structure
in combination with MgF_2 or LiF ^{that can be used} ~~as a material for the~~
20 ~~optical, additional films for the~~ ^{u 2} F_2 laser lithography.

Japanese Patent Application Laid-Open No. 2000-
89450 (Application No. 10-272570) suggests reticle
materials applicable to the F_2 laser lithography. They
are crystals of metal fluorides such as MgF_2 , LiF , and
25 CaF_2 , which are used so that their crystallographic axis
~~is~~ ^{is} oriented in a specific direction.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to provide optical, additional films (antireflection coatings, reflective coatings, protective coatings, etc.) and optical elements applicable to the F₂ laser lithography.

The inventor conducted extensive and intensive research in order to solve the above problems and succeeded in developing effective element techniques for [^]breakthrough improvement in performance of the optical systems of the optical apparatus such as the projection exposure apparatus, illumination apparatus, measurement apparatus, etc. used in the F₂ laser lithography and, in turn, ~~for~~ ^{ed} contribution to the improvement in microprocessing and productivity of semiconductors ~~and others~~.

One aspect of the present invention is a film comprising at least one layer of silica (SiO₂) containing fluorine (F).

In the film, preferably, a concentration of the fluorine in the layer or layers of silica is not less than 0.1 mol% (preferably, not less than 1 mol%) nor more than 10 mol%.

In the film, preferably, a refractive index of the layer or layers of silica for F₂ laser light is 1.60-1.80.

Preferably, the film comprises a layer a material

of which is selected from the group consisting of MgF_2 ,
LiF, and Na_3AlF_6 .

Another aspect of the invention is an optical
element wherein the film as set forth is added on a
5 surface thereof.

In the optical element, preferably, said optical
element is comprised of fluorite.

In the optical element, preferably, said optical
element is comprised of silica containing fluorine.

10 In the optical element, preferably, said film is
an antireflection coating.

Another aspect of the invention is an optical
apparatus for vacuum ultraviolet lithography,
comprising the optical element as set forth.

15 Another aspect of the invention is a device
fabrication method comprising a step of exposing a
wafer to a device pattern by the optical apparatus as
set forth, and a step of developing the wafer thus
exposed.

20

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of a BO lens;

Figs. 2A and 2B are cross-sectional views of an 8-
step BO lens;

25 Fig. 3 is a BO lens substrate before production of
a BO lens;

Fig. 4 is a cross-sectional view of a BO lens and

three masks used in production of the BO lens;

Fig. 5 is a cross-sectional view of a BO lens with antireflection coatings of the present invention deposited on a front surface and a back surface;

5 Fig. 6 is a cross-sectional view of a lens with antireflection coatings of the present invention;

Fig. 7 is a view showing a mirror with a reflective film of the present invention on a surface; and

10 Fig. 8 is a drawing showing an embodiment of the optical apparatus according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

We propose here that silica containing fluorine
15 (which will be also referred to hereinafter as " $\text{SiO}_2\text{:F}$ ") is used as a material for the optical films (additional films) (e.g., antireflection coatings, reflective coatings, or protective coatings) added on the substrate of the optical elements for the F_2 laser
20 lithography.

The inventor succeeded in dramatically raising the transmittance of silica films for the F_2 laser light by adding a predetermined amount of fluorine to the silica films. A nondoped silica film 1 μm thick has the
25 transmittance of not more than 10% for the F_2 laser light, whereas a silica film doped with about 1 mol% of fluorine has the transmittance raised to about 90% for

the F_2 laser light.

In general, ^{used in} ~~the~~ materials of the optical elements for photolithography are required to have ~~the~~ ^a transmittance of 90% or more for ^{specific} light of an objective wavelength. Silica films doped with fluorine have ~~transmittances higher~~ ^{greater} than ~~it~~ ^{that} for the F_2 laser light and thus can be used as materials ^{for} of the optical, additional films for the F_2 laser light.

The film of silica containing fluorine desirably
10 has the transmittance of 90% or more for the F_2 laser light of 157 nm when the thickness thereof is 1 μ m. Further, the transmittance is more desirably not less than 95% and most desirably not less than 99%.

The film of silica containing fluorine desirably
15 has at least the refractive index higher than that of fluorite. This is because the refractive index (n) of fluorite is about 1.56 for the F_2 laser light having the wavelength of 157 nm, and it becomes feasible to make a more efficient, optical, additional film, ² by employing
20 a layered structure with either of MgF_2 (n = 1.47), LiF (n = 1.49), and Na_3AlF_6 (n = 1.48) having the refractive indices lower than that of fluorite.

More specifically, the refractive index of the $SiO_2:F$ film is desirably 1.6 to 1.8.

25 As an example, the refractive index of the $SiO_2:F$ film containing 1 mol% of fluorine for the F_2 laser light is 1.65 and this $SiO_2:F$ film can be combined with

an LiF film or an MgF_2 film to obtain an efficient, optical, thin film (multilayer film) (reference is made to examples).

For using the silica containing fluorine ($\text{SiO}_2\text{:F}$)
5 as an antireflection coating or a reflective coating for the F_2 laser lithography, a content of fluorine in the silica film is desirably 0.1 mol% to 10 mol%.

When the concentration of fluorine is not less than 0.1 mol%, the silica film containing fluorine has
10 a practically allowable transmittance for the F_2 laser light. When the fluorine concentration is not more than 10 mol%, it is possible to maintain stable, optical characteristics (refractive index, transmittance, etc.) and film properties.

15 The fluorine content is more desirably in the range of not less than 1 mol% nor more than 10 mol%.

In the fluorine-containing silica as a material for the optical, additional films (antireflection coatings, reflective coatings, protective coatings) or
20 as a material for the optical elements, fluorine is desirably present everywhere ^{at} ~~in~~ a constant concentration. If fluorine is scattered ^{at} ~~in~~ a constant concentration ^{the} in in-plane and depth directions, there ^{not be any location-dependent} will ~~occur no~~ fluctuations in the optical
25 characteristics and film properties, including the refractive index and the transmittance, ~~depending upon~~ ^{locations}.

A method of forming the fluorine-containing silica film can be selected arbitrarily from well-known methods that can form the silica film and make the silica film contain fluorine in the aforementioned concentration range.

For example, such conventional methods include chemical vapor deposition (CVD), sputter deposition, ion beam sputtering deposition, reactive sputtering deposition, electron beam evaporation, and so on.

When the fluorine-containing silica ($\text{SiO}_2\text{:F}$) film is formed by these methods, it is important to avoid dispersion of fluorine concentration (in the in-plane and depth directions) in the film.

For example, when the film is formed by the reactive sputtering deposition method, a sputter target is desirably silica (SiO_2) or fluorine-containing silica ($\text{SiO}_2\text{:F}$). Sputter gas is desirably ^{an}inert gas (Ar, Ne, He, Kr, or the like) and reaction gas desirably fluorine gas (F_2).

When the film is formed by sputter deposition, it is desirable to preliminarily prepare a target of silica doped with fluorine ($\text{SiO}_2\text{:F}$) by another method, use ^{an}inert gas (Ar, Ne, He, Kr, or the like) as the sputter gas, and implement sputtering of the target.

In these film-forming methods ^{utilizing}~~making use of the~~ sputtering, ~~phenomenon~~₂ the composition of the deposited film often ~~disagrees with~~ the composition of the target

differs from

due to the
~~because of~~ influence of selective sputtering or the
like, ~~and it is~~ ^{it is} thus, desirable to supplement fluorine *in order*
~~so as~~ to obtain the film ^{with desired} in the objective fluorine
concentration.

5 One form of the optical, additional films
according to the present invention is a multilayer film
consisting of a stack of alternate films being a
combination of the fluorine-containing silica ($\text{SiO}_2\text{:F}$)
film with a metal fluoride, specifically, either of
10 MgF_2 , LiF , Na_3AlF_6 , CaF_2 , LaF_3 , BaF_2 , SrF_2 , and so on.

Particularly, the optical, additional films for
the F_2 laser lithography are more desirably ^a ~~of the~~ stack
structure of $\text{SiO}_2\text{:F}$ and LiF , Na_3AlF_6 , or CaF_2 films.

Examples of the stack structure of the optical,
15 additional films for the F_2 laser lithography will be
presented below. When the films are formed in ^a ~~a~~ two-
layer structure, desirable structures are MgF_2 (265
 \AA)/ $\text{SiO}_2\text{:F}$ (238 \AA)/fluorite (optical element), LiF (265
 \AA)/ $\text{SiO}_2\text{:F}$ (238 \AA)/fluorite (optical element), and
20 Na_3AlF_6 (265 \AA)/ $\text{SiO}_2\text{:F}$ (238 \AA)/fluorite (optical
element). The thickness of each layer indicated by
(... \AA) was determined according to the condition for *an*
interference film at 157 nm (the wavelength of F_2 laser
light).

25 When the films are formed in ^a ~~a~~ four-layer structure,
desirable structures are MgF_2 (434 \AA)/ $\text{SiO}_2\text{:F}$ (238
 \AA)/ MgF_2 (434 \AA)/ $\text{SiO}_2\text{:F}$ (238 \AA)/fluorite (optical

element), LiF (434 Å)/SiO₂:F (238 Å)/LiF (434 Å)/SiO₂:F (238 Å)/fluorite (optical element), and Na₃AlF₆ (434 Å)/SiO₂:F (238 Å)/Na₃AlF₆ (434 Å)/SiO₂:F (238 Å)/fluorite (optical element). The thickness of each layer was
5 also determined according to the condition for *an* interference film at 157 nm (the wavelength of F₂ laser light).

The optical, additional films of the present invention are not ~~limited to be added only~~ ^{to} on the
10 surfaces of lenses, but can also be added ^{to the} on surfaces of diffraction gratings, mirrors, and filters, whereby a remarkable effect ~~can be expected~~ ^{to} improvement in diffraction efficiency and ^{an} increase ⁱⁿ of reflectance.

These optical elements (diffraction gratings,
15 lenses, mirrors, filters) with the optical, additional films are also one aspect of the present invention.

The optical apparatus using these optical elements as components are also one aspect of the present invention. The optical apparatus herein embraces the
20 projection exposure apparatus, illumination apparatus, measurement apparatus, and so on used in the F₂ laser lithography.

The present invention will be described hereinafter in further detail with examples thereof.
25 *g* Example 1 *g*

A circular BO (Binary Optics) lens having the diameter of 20 mm was made.

The BO lens herein is a kind of diffraction grating and the diffraction grating is normally used as a spectroscopic element of a spectroscope in the optical apparatus for fabrication of semiconductors.

5 The BO lens has a ^{stepwise} diffraction grating and is expected to be applied to optical systems using ultraviolet light because of its potential ^{of} achromatism and ^{an} aspheric effect.

The present BO lens is designed to work at the
10 wavelength of the F₂ laser light of 157 nm and has about 1800 rings. Each ring has a ^{stepwise} structure of eight steps.

Fig. 1 and Figs. 2A and 2B are schematic views of the BO lens and the ^{stepwise} structure of the rings
15 thereof, respectively. The outermost ring has such designed values, that the width of each step is 0.35 μm , the height of each step 0.04 μm , and the width and height of the ring are 2.8 μm and 0.28 μm , respectively. Fig. 2A is a partial magnification of
20 Fig. 2B.

This BO lens was fabricated in such a way that, ^{with a} ~~a~~ ^{fluorite} substrate 1 ~~of fluorite having the~~ diameter of 2 inches and ^a ~~the~~ thickness of 4 mm, as shown in Fig. 3, was prepared. Patterns of chromium masks (11 to 13) having
25 different intervals were successively printed as reduced images in respective, negative photoresists coated on the substrate 1, using a stepper for

KrF ($\lambda = 248 \text{ nm}$) ^{ins} Each photoresist was developed after printed to obtain a resist pattern, and the substrate 1 was etched by a dry etching method using the resultant resist patterns as masks. Gas for the dry etching was
5 a mixture of argon and hydrogen.

Fig. 4 is an explanatory drawing simultaneously showing the three masks (11 to 13) successively used for the fabrication of the present BO lens, together with the lens. The above process was repeated three
10 times while changing the masks, thereby making the BO lens of the stepwise structure with rings each consisting of eight steps.

In the present invention, antireflection coatings consisting of alternate layers of SiO_2 :F layers were
15 laid on the front surface and on the back surface of the BO element fabricated as described above (Fig. 5).

The coatings were formed by the reactive sputtering deposition method. The sputtering target was a synthetic quartz sheet. The film-forming system
20 was a sputtering deposition system of ^a RF type (model SBR-110 available from Ulvac Inc.).

The sputtering deposition was carried out under the conditions ^{described in} of Table 1.

In order to evaluate the physical properties of the SiO_2 :F films of the present invention, a ~~substrate~~
25 ^{substrate} of flat plate ~~shape~~ (hereinafter referred to as a test sample) made of the same material as the BO element was

also introduced into the deposition chamber and subjected to deposition at the same time.

TABLE 1

Deposition Conditions	Values
sputtering target	SiO ₂
pressure in deposition chamber	4 Pa
substrate temperature (temperature of BO element)	22° C
sputter gas and reaction gas	10vol%F ₂ -containing Ar gas, 20 sccm
deposition time	7.6 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

Evaluation was made for the physical properties of the SiO₂:F films thus deposited on the BO element. This evaluation ~~for~~^{of} the physical properties was conducted with the test sample.

Cross-sections of the test sample were observed with a scanning electron microscope, and it was found from the observation that the thickness of the SiO₂:F films was 238 Å.

The concentration of fluorine (F) in the SiO₂:F films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%.

Further, a depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of F in the depth direction in the $\text{SiO}_2\text{:F}$ films, and it was verified that F was distributed ^{at} in a constant concentration in the $\text{SiO}_2\text{:F}$ films.

The refractive index of the $\text{SiO}_2\text{:F}$ films was measured at the wavelengths of 200 to 300 nm with an ellipsometer and the refractive index was approximately 1.65 for the F_2 laser light (at the wavelength of 157 nm) from extrapolation of the measurement results.

After completion of the deposition of the $\text{SiO}_2\text{:F}$ films, lithium fluoride (LiF) was then deposited subsequently without taking the substrate out of the deposition system. The deposition conditions are presented in Table 2.

TABLE 2

Deposition Conditions	Values
sputtering target	LiF
pressure in deposition chamber	2 Pa
substrate temperature (temperature of BO element)	22° C
sputter gas and reaction gas	10vol% F_2 -containing Ar gas, 10 sccm
deposition time	9.7 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The physical properties of the LiF films thus deposited were also evaluated with the test sample.

Cross-sections of the test sample were observed with the scanning electron microscope and the thickness of the LiF film was 263 Å.

The diffraction efficiency of this BO element was measured with a diffraction efficiency measuring system, and the BO element demonstrated an ^{average} improvement of 14% ~~on average~~ in the diffraction efficiency, as compared with elements without the antireflection coatings.

Example 2

Antireflection coatings 5 having the structure of "MgF₂/SiO₂:F/lens surface" were deposited on surfaces of a fluorite lens 2 for the F₂ laser light having the wavelength of 157 nm (Fig. 6). The lens 2 is ~~a lens~~ for the F₂ lithography, ^{it} and has ^a the lens diameter of 100 mm and ^{its largest} the thickness of 10 mm ^{is} ~~in the thickest portion~~.

In the present example, ^{238 Å thick} the SiO₂:F films were deposited ~~in the thickness of 238 Å~~ by sputtering a target of fluorine-containing silica by RF sputtering. The deposition conditions of the SiO₂:F films in the present example are presented in Table 3.

TABLE 3

Deposition Conditions	Values
sputtering target	SiO ₂ :F
pressure in deposition chamber	2 Pa
substrate temperature (temperature of lens)	22° C
sputter gas and reaction gas	Ar gas, 10 sccm
deposition time	6.9 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The concentration of fluorine (F) in the SiO₂:F films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%. Further, the depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of fluorine in the depth direction in the SiO₂:F films, and it was verified that fluorine was distributed ^{at} in a constant concentration in the SiO₂:F films.

The refractive index of the SiO₂:F films was measured at the wavelengths of 200 to 300 nm with the ellipsometer, and the refractive index was approximately 1.65 at the wavelength of 157 nm of the F₂ laser light from ^{an} extrapolation of the measurement results.

263 Å thick

Further, [^]magnesium fluoride (MgF_2) films were deposited as upper layers ~~in the thickness of 263 Å~~ by similar means. The deposition conditions at that time are presented in Table 4.

TABLE 4

Deposition Conditions	Values
sputtering target	MgF_2
pressure in deposition chamber	2 Pa
substrate temperature (temperature of lens)	22° C
sputter gas and reaction gas	Ar gas, 10 sccm
deposition time	19 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

Similarly, an antireflection coating 5 of two layers was also laid on the back surface of the lens 2.

The transmittance of the complete lens was measured for the F_2 laser light of 157 nm, and the transmittance ~~was~~ improved by about 8% ~~in the central~~ part.

at in the central portion

Example 3)

A film having the structure of " $\text{MgF}_2/\text{SiO}_2\text{:F/mirror}$ surface" was laid as a reflective coating 6 on a surface of a reflecting mirror used in an optical path

of a spectrophotometer (Fig. 7).

A fluorine-containing silica ($\text{SiO}_2\text{:F}$) film was deposited as a reflective coating 6 ^{265 Å thick} ~~in the thickness of 265 Å~~ on an aluminum (Al) deposited film 4 formed on a glass substrate 3, using the sputtering system similar to that used in Example 1. The thickness (265 Å) of this film 6 was determined from the condition of the interference film for rays of 157 nm.

The deposition conditions of the $\text{SiO}_2\text{:F}$ film are the same as in Example 1.

The deposition conditions of the MgF_2 film are presented in Table 5.

TABLE 5

Deposition Conditions	Values
sputtering target	MgF_2
pressure in deposition chamber	2 Pa
substrate temperature (temperature of reflecting mirror)	22° C
sputter gas and reaction gas	10vol% F_2 -containing Ar gas, 10 sccm
deposition time	11.1 min
frequency of applied RF power	13.56 MHz
applied RF power	100 W

The reflectance of the reflection-enhanced mirror (Fig. 7) obtained in this ^{manner} way was measured, and it was verified that the reflectance was enhanced by 7% at the angle of incidence of 45° for the F_2 laser light.

5 There was no ^{alternative} choice but to use an Al film in an exposed state for the conventional mirrors for the F_2 laser light. The reason was that if an optical, additional film was laid on the surface, the reflectance of the mirror was ^{substantially decreased} heavily lowered. For this reason, ^{useful} lives of ~~the~~ ^{are} conventional mirrors were short, and these mirrors ^{have} had to be replaced frequently.

10 However, it became feasible to ~~extend~~ ^{at least double} the ^{useful} life of the ^{conventional} mirror ~~to double or more those of the conventional mirrors~~. by laying the optical, additional film of the present invention on the surface of the Al mirror.

15 Example 4

The lens of the same shape as in Example 3 was made of ~~a material of~~ silica containing 4 mol% of fluorine ($SiO_2:F$). Further, antireflection coatings 5 having the stack structure of four layers of "LiF/ $SiO_2:F$ /LiF/ $SiO_2:F$ /lens surface" ^{was, still} were formed on the lens surfaces (on the front surface and on the back surface). The deposition conditions of $SiO_2:F$ and LiF were the same as in Example 1.

25 The concentration of fluorine (F) in the $SiO_2:F$ films was evaluated by Raman spectroscopy, and the fluorine concentration was approximately 1 mol%.

Further, the depth profile analysis by SIMS (Secondary ion mass spectrometry) was performed to obtain a profile of fluorine in the depth direction in the $\text{SiO}_2\text{:F}$ films, and it was verified that fluorine was distributed ^{at} ~~in~~ a constant concentration in the $\text{SiO}_2\text{:F}$ films.

The refractive index of the $\text{SiO}_2\text{:F}$ films was also measured at the wavelengths of 200 to 300 nm with the ellipsometer, and the refractive index was approximately 1.65 at the wavelength of 157 nm of the F_2 laser light from extrapolation of the measurement results.

The transmittance of the lens of the present example was measured for the F_2 laser light, and it was verified therefrom that the transmittance was improved by about 8%.

✓ Example 5 ✓

The optical, additional films were made by resistance heating evaporation, instead of the film forming methods of the fluorine-containing silica ($\text{SiO}_2\text{:F}$) films, magnesium fluoride (MgF_2) films, and lithium fluoride (LiF) films in Examples 1, 2, and 3. The present example also confirmed the improvement in the diffraction efficiency of the BO lens, the improvement in the transmittance of the lens, and the enhancement of reflectance of the mirror as in Examples 1, 2, and 3.

✓ Example 6 ✓

The antireflection coatings as made in Example 5 were laid on surfaces of optical elements (lenses, mirrors, diffraction gratings) used in the optical systems of the projection exposure apparatus (steppers

5 or scanners) for fabrication of semiconductors using the F_2 laser for printing. As a result, the lenses

demonstrated ^{about an 8%} the increase of ~~about 8%~~ in the

transmittance. ^{showed about at 8%} The mirrors ^{the increase of about 8%} in

~~the reflectance~~ and the diffraction gratings ^{demonstrated an about 15%} the

10 increase of ~~about 15%~~ in the diffraction efficiency.

Fig. 8 is a schematic view of this projection exposure apparatus. The optical, additional films of the

present invention are used in the optical elements of its illumination system and/or in the optical elements

15 of its projection system and/or in the optical elements of masks and the like.

The transmittance of the entire projection exposure apparatus was improved for the F_2 laser light by virtue of the effect of the optical, additional

20 films laid on these optical elements ^{and it} ~~and it~~ Thus, ^{it} became feasible to fabricate the semiconductor devices ~~in at a~~ ^{greater} higher density than before.

WHAT IS CLAIMED IS:

1. A film comprising at least one layer of silica containing fluorine.
- 5 2. The film according to Claim 1, wherein a concentration of the fluorine in the layer or layers of silica is not less than 0.1 mol% nor more than 10 mol%.
- 10 3. The film according to Claim 2, wherein said concentration of the fluorine is not less than 1 mol%.
- 15 4. The film according to Claim 1, wherein a refractive index of the layer or layers of silica for F_2 laser light is 1.60 to 1.80.
- 20 5. The film according to Claim 1, comprising a layer a material of which is selected from the group consisting of MgF_2 , LiF , and Na_3AlF_6 .
- 25 6. An optical element wherein the film as set forth in any one of Claims 1 to 5 is added on a surface thereof.
7. The optical element according to Claim 6, wherein said element is comprised of fluorite.
8. The optical element according to Claim 5,

wherein said element is comprised of silica containing fluorine.

9. The optical element according to Claim 6,
5 wherein said film is an antireflection coating.

10. An optical apparatus for vacuum ultraviolet lithography, comprising the optical element as set forth in Claim 6.
10

11. An optical apparatus for vacuum ultraviolet lithography, comprising the optical element as set forth in any one of Claims 7 to 9.

12. A device fabrication method comprising a step
15 of exposing a wafer in a device pattern by the optical apparatus as set forth in Claim 10, and a step of developing the wafer thus exposed.

13. A device fabrication method comprising a step
20 of exposing a wafer in a device pattern by the optical apparatus as set forth in Claim 11, and a step of developing the wafer thus exposed.

ABSTRACT OF THE DISCLOSURE

A monolayer or multilayer film has a single layer or multiple layers of silica containing fluorine. An optical element has the forgoing film laid on a surface of a substrate. A concentration of the fluorine in the layer or layers of silica is not less than 0.1 mol% (preferably, not less than 1 mol%) nor more than 10 mol%.